MICROWAVE MEASUREMENTS OF THE ELECTRIC DIPOLE MOMENT AND OTHER DIELECTRIC PROPERTIES OF NITROBENZENE

by

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INTRODUCTION

During the past twenty years the use of microwaves as a research tool has been investigated extensively. Roberts and von Hippel (15) did some of the early work in the use of microwaves to determine dielectric properties. Their method utilized the reflection of microwaves inside cylindrical waveguides. Variations and refinements aimed at simplifying the mathematics and improving the experimental techniques (16) (3) (10) (20) have since appeared.

Once the complex dielectric constant of a dielectric is known, the theory developed by Debye (4) showing the relationship between complex dielectric constant, the electric dipole moment and the relaxation time could be used to determine the latter two quantities. The dipole moment and relaxation time are of particular interest to the physical chemist studying molecular structure and behavior.

The method described in this paper is a variation of the one used by Roberts and von Hippel. Windle's (20) solution to the impedance equation was used in conjunction with a digital computer to determine the complex dielectric constant, dipole moment and relaxation time for various concentrations of a polar liquid in a non-polar solvent.

An empirical correction factor was added to the measured optical index of refraction to correct it to the index in the far infrared generally found by extrapolation of the sodium D line to "infinite wavelength" by use of a dispersion formula. The dipole moment was thus brought within the range of values determined by other methods.

THEORY

In general when a nonconducting substance or dielectric is placed between the plates of a capacitor, the capacitance is found to be greater than when vacuum is the dielectric. The ratio of the capacitance with the dielectric in place to the capacitance of a vacuum capacitor is called the dielectric constant k of the dielectric,

$$\frac{C_{die}}{C_{vac}} = k \tag{1}$$

When a rapidly alternating electric field is applied to the capacitor containing the dielectric, a charging current 90° out of phase with the applied voltage and a loss current in phase with the applied voltage are found to flow. A complex dielectric constant k^* is then introduced such that

$$k^* = k' - j\,k'' \tag{2}$$

where k' is now called the dielectric constant and k'' is the loss factor and the ratio of k'' to k' is the loss tangent:

$$\tan \delta = \frac{k''}{k'} \tag{3}$$

For static and low frequency electric fields for which the polarization is in phase with the applied field, a physical capacitor may be set up and the change in capacitance as the dielectric is introduced may be readily determined and the dielectric constant directly computed by use of equation (1). However, for fields in the microwave frequency range the phase difference between the potential and true charges on the capacitor make it impossible to use equation (1) to find k^* (1) and other methods of finding k^* must be utilized. Roberts and von Hippel (15) developed a method whereby the reflection properties of microwaves

in wave guides would yield the complex dielectric constant, loss factor and loss tangent.

Let an electromagnetic wave traveling in the x direction in a wave guide strike the interface between two media and let the first medium (medium 1) be air and the second medium be the dielectric for which the dielectric properties are to be determined. The interface between the air and dielectric is at x = 0 and the dielectric is terminated by a metal short at x = d. A standing wave pattern is set up in both media; let x_o be the magnitude of the distance from the interface to the first minimum of the electric field in the air filled wave guide. Assuming a non-magnetic dielectric and a loss free medium 1, Roberts and von Hippel obtained the impedance equation,

$$\frac{\tanh \gamma_2 d}{\gamma_2 d} = \frac{1}{j \beta_1 d} \cdot \frac{(E_{min}/E_{max}) - j \tan \beta_1 x_o}{1 - j(E_{min}/E_{max}) \tan \beta_1 x_o}. \qquad (4)$$

The subscripts refer to the media, γ is the propagation factor, E_{min}/E_{max} the inverse voltage standing wave ratio in the air filled guide and $\beta = 2\pi/\lambda$ the phase factor. γ and β are related by

$$\gamma = \alpha + j \beta \qquad (5)$$

where α is called the attenuation factor.

Crawford (3) expressed a relation between γ_2 and k^*,

$$k^* = \frac{(1/\lambda_c)^2 - (\gamma_2/2\pi)^2}{(1/\lambda_f)^2} = \frac{(1/\lambda_c)^2 - (\gamma_2/2\pi)^2}{(1/\lambda_c)^2 - (1/\lambda_1)^2}. \qquad (6)$$

λ_c is the cutoff wavelength, λ_f is the free space wavelength and λ_1 is the wavelength in the air filled wave guide. Thus, a solution of the impedance equation (4) and determination of the λ's is required to obtain k^*.

Major (8) has shown the inverse voltage standing wave ratio may be expressed as

$$\frac{E_{min}}{E_{max}} = \frac{\sin \pi \Delta x/\lambda_1}{\left[(E(x_1)/E_{min})^2 - \cos^2 \pi \Delta x/\lambda_1\right]^{1/2}} \tag{7}$$

where Δx is the distance between the positions of twice the minima of the electric field in medium 1, $x_1 = x_{min} \pm \Delta x/2$ and x_{min} is the position of E_{min} from the interface. A probe in a section of slotted wave guide is often used to determine the field inside the wave guide. Windle (20) assumed the probe to contain a crystal detector of response law n. When the ratio of the voltage from the detector at x_1 to that at x_{min} was set at 2, he obtained

$$\frac{E_{min}}{E_{max}} = \frac{\sin \pi \Delta x/\lambda_1}{(4^{1/n} - 1 + \sin^2 \pi x/\lambda_1)^{1/2}} \tag{8}$$

Windle (20) solved the impedance equation by iteration as follows. Equation (8) was substituted into equation (4) and the left side of equation (4) was transformed and expanded in terms of trigonometric functions, with $\alpha_2 d = X$ and $\alpha_2 d = Y$. The right side of equation (4) was simplified by setting it equal to $A + j\,B$. After rationalization, the real part of the left side of equation (4) minus A was set equal to $f(X,Y) = 0$ and the imaginary part minus B was set equal to $g(X,Y) = 0$. After expansion in a first order Taylor series in two variables, for an initial guess of $X = X_0$ and $Y = Y_0$ one obtains

$$\begin{aligned} f(X_1,Y_1) &= f(X_0,Y_0) + h\frac{\partial f}{\partial x} + h\frac{\partial f}{\partial y} \\ g(X_1,Y_1) &= g(X_0,Y_0) + h\frac{\partial g}{\partial x} + h\frac{\partial g}{\partial y} \end{aligned} \tag{9}$$

For a solution, X_1 and Y_1 must be found such that $f(X_1,Y_1) = g(X_1,Y_1) = 0$. By setting equations (9) equal to zero one obtains for h and k

$$h = \frac{-f(X_o,Y_o)\frac{\partial g}{\partial y} + g(X_o,Y_o)\frac{\partial f}{\partial y}}{\frac{\partial f}{\partial x}\frac{\partial g}{\partial y} - \frac{\partial f}{\partial y}\frac{\partial g}{\partial x}}$$

$$k = \frac{-g(X_o,Y_o)\frac{\partial f}{\partial x} + f(X_o,Y_o)\frac{\partial g}{\partial x}}{\frac{\partial f}{\partial x}\frac{\partial g}{\partial y} - \frac{\partial f}{\partial y}\frac{\partial g}{\partial x}} \qquad (10)$$

and

$$\frac{\partial f}{\partial x} = \frac{\partial g}{\partial y} = (1 - A)\cos Y \cosh X - (AX - BY)\cos Y \sinh X$$
$$+ (AY + BX)\sin Y \cosh X + B \sin Y \sinh X$$
$$\frac{\partial g}{\partial x} = -\frac{\partial f}{\partial y} = (1 - A)\sin Y \sinh X - (AX - BY)\sin Y \cosh X \qquad (11)$$
$$- (AY + BX)\cos Y \sinh X - B\cos Y \cosh X$$

By iteration a solution for $\gamma_2 = \alpha_2 + j\beta_2$ of equation (4) may be obtained to the accuracy desired. k^* is then found from equation (6).

Debye (4) was the first to successfully relate the dielectric constant to the dipole moment μ of a polar molecule. The Debye equation is given as

$$P_m = \frac{k^* - 1}{k^* + 2}\frac{M}{\rho} = \frac{4\pi}{3}N\alpha + \frac{4\pi N}{9kT}\mu^2 \qquad (12)$$

P_m is called the polarization. The first term on the right is the Clausius-Mossotti expression for non polar dielectrics

$$\frac{k^* - 1}{k^* + 2}\frac{M}{\rho} = \frac{4\pi}{3}N\alpha \qquad (13)$$

where M is the molecular weight, ρ is the density, N is Avogadro's number and α is the polarizability.

The second term on the right side of equation (12) is derived from the Boltzmann principle for the relative probability of a dipole μ in an element of volume making an angle θ with the direction of the electric field E. The average value of the component of μ in the direction of E is given by (13)

$$\bar{\mu} = \frac{\int_0^{2\pi}\int_0^{\pi} \mu \cos\theta \, e^{\mu E \cos\theta/KT} \sin\theta \, d\theta \, d\phi}{\int_0^{2\pi}\int_0^{\pi} e^{\mu E \cos\theta/KT} \sin\theta \, d\theta \, d\phi}$$

where K is Boltzmann's constant and T is the absolute temperature.

Equation (12) is rewritten to include high frequency effects (generally above one megacycle per second) as

$$\frac{k^* - 1}{k^* - 2}\frac{M}{\rho} = \frac{4\pi N}{3}\left(\alpha + \frac{\mu^2}{3KT(1 + j\omega\tau)}\right). \qquad (14)$$

Here, ω is the angular frequency and τ is the relaxation time defined as the time in which the polarization decreases to 1/e of its original value after the electric field has been removed.

The first term on the right of equation (14) is the contribution to the total polarization due to induced polarization P_i. When an electric field is applied to the dielectric, the electrons, and to some extent the atoms of the molecules are slightly displaced. Thus, in the absence of permanent dipoles or in the presence of fields so high in frequency permanent dipoles cannot follow, the polarization $P_m = P_i = P_e + P_a$ where P_e is the electronic polarization and P_a is the atomic polarization. Under these conditions the second term on the right side of equation (14) is zero giving a method for determining α as k' approaches n^2, the square of the optical index of refraction where oscillating electrons can still contribute to the dielectric constant. We have

$$\frac{k' - 1}{k' + 2} = \frac{4\pi}{3} \alpha = \frac{n^2 - 1}{n^2 + 2} \qquad (15)$$

P_1 and α are then found from equation (15).

Electronic polarization is a process having a relaxation time of about 10^{-15} seconds and atomic polarization about 10^{-12} to 10^{-14} seconds, while for small molecules in liquids of low viscosity the time required is about 10^{-10} to 10^{-11} seconds (16). To find P_1, then, the index of refraction in the infrared region must be used, at a frequency too large for permanent dipole orientation but appreciably smaller than any vibration or rotation frequency (12) so as to avoid an anomalous dispersion region.

In practice it is quite difficult to obtain a refractive index value at a frequency which will satisfy the above requirements. Many substances have strong absorption bands in the infrared and hence dispersion may limit the usefulness of a refractive index measurement. To see this, consider the case of the characteristic frequency ω_0 of an electron elastically bound to an isolated atom (1). There is an elastic restoring force proportional to the displacement, s, of the electron, a damping force proportional to its velocity, and an additional force due to an external electric field of a linearly polarized light wave of intensity $Ee^{j\omega t}$. The equation of motion is

$$m\frac{d^2s}{dt^2} + m\gamma\frac{ds}{dt} + m\omega_0^2 s = -e_0 Ee^{j\omega t} \qquad (16)$$

where m is the mass of an electron, e_0 is its charge and γ is the damping constant.

A solution is

$$s = se^{j\omega t}$$

which leads to

$$a = -\frac{e_0 E}{m(\omega_0^2 - \omega^2 + j\gamma\omega)}$$

In the steady state

$$s = -\frac{e_0 E e^{j\omega t}}{m(\omega_0^2 - \omega^2 + j\gamma\omega)} \tag{17}$$

The $j\gamma\omega$ in the denominator means the elongation is not in phase with the alternating field.

To show more explicitly the phase difference equation (17) may be written as

$$s = -\frac{1}{m}\frac{e_0 E e^{j(\omega t - \delta)}}{\sqrt{(\omega_0^2 - \omega^2)^2 + \gamma^2\omega^2}} \tag{18}$$

and the phase difference δ is given by

$$\tan\delta = \frac{\gamma\omega}{\omega_0^2 - \omega^2}$$

The induced dipole moment is

$$p = \alpha E e^{j\omega t} = -se_0 \tag{19}$$

where α is the polarisability of equation (13). Thus

$$\alpha = -\frac{se_0}{Ee^{j\omega t}} \tag{20}$$

Combining equations (17) and (20) we have

$$\alpha = \frac{e_0^2}{m}\frac{1}{\omega_0^2 - \omega^2 + j\gamma\omega} \tag{21}$$

Now using the Maxwell relation and that for a gas at normal pressure the refractive index differs only slightly from 1, equation (13) may be written

$$n^* = 1 + 2nN_1\alpha \tag{22}$$

where N_1 is the number of particles of the i^{th} kind per cm^3. Combining equations (21) and (22) we have

$$n^* = 1 + \frac{2\pi N_1 e_o^2 (\omega_o^2 - \omega^2 - j\gamma\omega)}{m\left[(\omega_o^2 - \omega^2)^2 + \gamma^2\omega^2\right]} \tag{23}$$

Thus, it is seen n^* decreases each time ω increases through and becomes far removed from a resonance frequency ω_o.

The above discussion indicates, then, that the induced polarization in a gas may be evaluated approximately from the Clausius-Mossotti equation by using $k^* = n^{*2}$, measuring the refractive index at a visible wavelength such as the sodium D line and then by use of a dispersion formula such as equation (23) extrapolate to "infinite wavelength" in the far infrared, far from an absorption band. Another dispersion formula must be used for high pressure gases or for liquids or solids.

Although the refractive index n^* in equations (22) and (23) is a complex number $n^* = n_{real}(1 - jk)$, where k in this case is the absorptive index, with little loss in accuracy the Debye equation (24) may be written as

$$\frac{k^* - 1}{k^* + 2} = \frac{n_D^2 - 1}{n_D^2 + 2} + \frac{4\pi N_1 \mu^2}{9KT(1 + j\omega\tau)} \tag{24}$$

The refractive index for the sodium D line, n_D, is readily determined and is often used in equation (24). But n_D is not the correct refractive index for the frequency used to determine k^* and hence equation (24) is an approximation and a dispersion formula is sometimes used to compensate for n_D. Another method of adjusting n_D to the value required by equation (24) is described later.

Rationalizing equation (24) and equating real and imaginary parts, Crawford (3) obtained

$$\mu^2 = \frac{9KT(R - P)\left\{1 + \left[FI/(R - P)\right]^2\right\}}{\ln N_1} \tag{25}$$

and

$$\tau = \frac{FI}{\omega (R - P)} \tag{26}$$

where

$$R = \frac{k'^2 + k' + k''^2 - 2}{(k' + 2)^2 k''^2}$$

$$FI = \frac{3k''}{(k' + 2)^2 + k''} \quad \text{and} \quad P = \frac{n^2 - 1}{n^2 + 2} \tag{27}$$

The quantities K, T, N_1, n and ω are known or are measured, and k' and k'' are calculated by means of equations (4), (5) and (6). Hence the magnitude of the average dipole moment and the relaxation time may now be computed.

Plate I is the computer[1] flow chart used in the solution of equations. Fortran programing was used to solve the equations, average the results in sets of five, and to compute the average deviation of the results. Plate II is the Fortran language program.

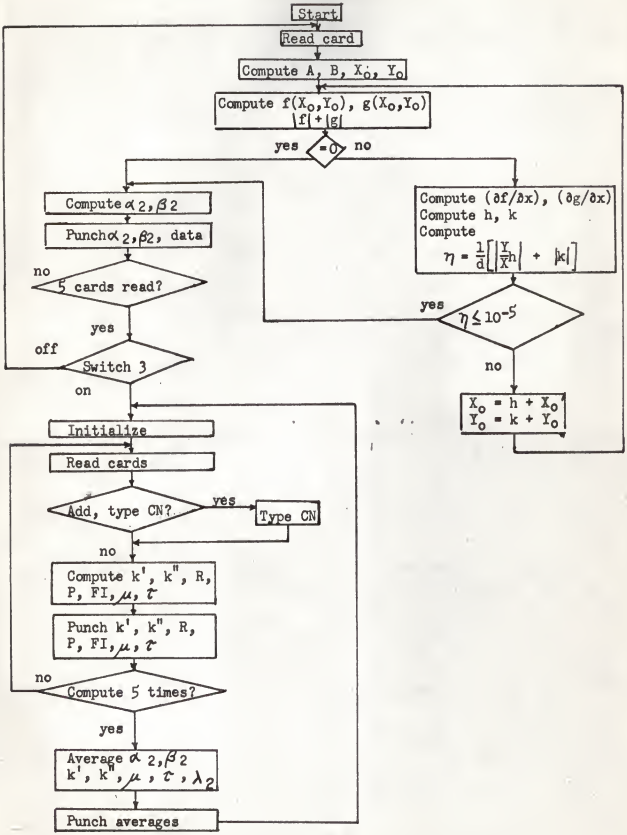
---

[1]The computer used was an IBM type 1620 data processing machine with floating decimal arithmetic.

PLATE I

Flow chart for computer program

PLATE I


Start
Read card
Compute A, B, X_o, Y_o
Compute $f(X_o,Y_o)$, $g(X_o,Y_o)$
$|f|+|g|$
yes
=0
no
Compute α_2, β_2
Punch α_2, β_2, data
no
5 cards read?
yes
off
Switch 3
on
Initialize
Read cards
Add, type CN?
yes
Type CN
no
Compute k', k", R, P, FI, μ, τ
Punch k', k", R, P, FI, μ, τ
no
Compute 5 times?
yes
Average α_2, β_2 k', k", μ, τ, λ_2
Punch averages
Compute $(\partial f/\partial x)$, $(\partial g/\partial x)$
Compute h, k
Compute
$\eta = \frac{1}{d}\left[\left|\frac{Y}{X}h\right| + |k|\right]$
yes
$\eta \leq 10^{-5}$
no
$X_o = h + X_o$
$Y_o = k + Y_o$

EXPLANATION OF PLATE II

Symbols used in programing are:

* means multiplication

ID = identification number.

CLMDA = cutoff wavelength λ_c in cm.

D = dielectric thickness d in cm.

TEMP = absolute temperature T.

DX = distance Δx in cm. between two positions of twice E_{min} in air.

XO = distance x_o in cm. from interface to first E_{min} in air.

REFI = refractive index n_D for sodium D line

PDEN = particle density N_1

E = $\frac{E_{min}}{E_{max}}$

DFX = $\left(\frac{\partial f}{\partial x}\right)_y$ and DGX = $\left(\frac{\partial g}{\partial x}\right)_y$

ALP2 = α_2, BET2 = β_2

CN = correction to be added to n_D.

FSLSQ = square of free space wavelength λ_f.

PK1 = k', PK2 = k''

DPM = μ, TAU = τ

ALMD2 = average λ_2

A prefix of the letter A on the above quantities refers to the average of that quantity.

4.5320 = λ_1

1.1420 = $4^{1/n} - 1$

3.2065 = λ_f

39.4784 = $4n^2$

1.38026E - 16 = Boltzmann's constant K

9.34E + 09 = frequency of 9.329 kilo megacycles per sec.

PLATE II

```
ENTER SOURCE PROGRAM, PUSH START
      C      PROGRAM TO COMPUTE DIPOLE MOMENT
      C      PART ONE, PROGRAM SWITCH 4 ON FOR TRACE
      C      PROGRAM SWITCH 3 ON TO GO TO PART TWO
         8 J = 1
         1 FORMAT (1H,F6.0,F10.0,F10.0,F10.0,F10.0,F10.0,E11.8)
         5 READ 1,ID,CLMDA,D,TEMP,DX,XO,REFI,PDEN
           J=J+1
           C=SIN(3.1H159*DX/4.532)
           E = C/SQRT(1.1H20+C*C)
           B1=2.0*3.1H159/4.5320
           SINE=SIN(B1*XO)
           DEN=(B1)*D*((E*E-1.0)*SIN(B1*XO)*SIN(B1*XO)+1.0)
           A=0.5*(E*E-1.0)*SIN(2.0*B1*XO)/DEN
           B=-E/DEN
           X=0.02*D
           Y=2.7*D
           Y=2.7*D
         3 SINHX=(EXP(X)-1.0/EXP(X))/2.0
           COSHX=(EXP(X)+1.0/EXP(X))/2.0
           F=COS(Y)*SINHX-(A*X-B*Y)*COS(Y)*COSHX+(A*Y+B*X)*SIN(Y)*SINHX
           G=SIN(Y)*COSHX-(A*Y+B*X)*COS(Y)*COSHX-(A*X-B*Y)*SIN(Y)*SINHX
           IF(SQRT(F*F)+SQRT(G*G))6,11,6
         6 DFXA=(1.0-A)*COS(Y)*COSHX-(A*X-B*Y)*COS(Y)*SINHX
           DFXB=(A*Y+B*X)*SIN(Y)*COSHX+B*SIN(Y)*SINHX
           DFX=DFXA+DFXB
           DGXA=(1.0-A)*SIN(Y)*SINHX-(A*X-B*Y)*SIN(Y)*COSHX
           DGXB=-(A*Y+B*X)*COS(Y)*SINHX-B*COS(Y)*COSHX
           DGX=DGXA+DGXB
           HH=(-F*DFX-G*DGX)/(DFX*DFX+DGX*DGX)
           HK=(-G*DFX+F*DGX)/(DFX*DFX+DGX*DGX)
           ETA=(SQRT(X*Y*HH*HH/(X*X))+SQRT(HK*HK))/D
           IF(ETA-.00001)11,11,55
        55 CONTINUE
           X=X+HH
           Y=Y+HK
           GO TO 3
        11 ALP2=X/D
           BET2=Y/D
        61 FORMAT(1H,F10.5,E14.8,E14.8,E14.8,E14.8)
           PUNCH 61,ID,CLMDA,ALP2,BET2,REFI,PDEN
           PUNCH 61,ID,SINE,E,C,A,B
         2 FORMAT(1H,E14.8,E14.8)
           PUNCH 2,ID,TEMP,SINE
           IF(J-6)5,4,4
         4 IF(SENSE SWITCH 3)26,8
      C    DIPOLE MOMENT PART TWO
      C    PROGRAM SWITCH 1 ON FOR REFRACTIVE INDEX CORRECTION
      C    SWITCH 2 ON TO CORRECT REFRACTIVE INDEX
      C    PROGRAM SWITCH 3 ON TO ADD +.001 TO REFRACTIVE INDEX CORRECTION
        26 CN=0.0
        25 Z=5.0
```

PLATE II CONTINUED

```
      AA=0.0
      AB=0.0
      AE=0.0
      AFI=0.0
      AF2=0.0
      AD=0.0
      AT=0.0
      J=1
    9 READ 61,ID,CLMDA,ALP2,BET2,REFI,PDEN
      READ 61,ID,SINE,E,C,A,B
      READ 2,ID,TEMP
      J=J+1
      IF (SENSE SWITCH 1)24,7
   24 IF (SENSE SWITCH 2)100,200
  100 IF (SENSE SWITCH 3)90,95
   90 CN=CN+0.001
      GO TO 53
   95 CN=CN-0.001
   52 FORMAT(31H REFRACTIVE INDEX CORRECTION = E14.8/)
   53 PRINT 52,CN
  200 REFI=REFI+CN
    7 FSLSQ=3.2065*3.2065
      FK1=((1.0/(CLMDA*CLMDA))+(BET2*BET2-ALP2-ALP2)/39.4784)*FSLSQ
      FK2=2.0*ALP2*BET2-FSLSQ/(4.0*3.14159*3.14159)
      R=(FK1*FK1+FK1+FK2*FK2-2.0)/((FK1+2.0)*(FK1+2.0)+FK2*FK2
      P=(REFI*REFI-1.0)/(REFI*REFI+2.0)
      FI=3.0*FK2/((FK1+2.0)*(FK1+2.0)+FK2)
      DPMSB=1.0+(FI/(R-P))*(FI/(R-P)
      DPM=SQRT((1.0/(12.5663*PDEN))*(9.0*1.38026E-16)*TEMP*(R-P)*DPMSB)
      OMEGA=6.2832*0.3E+09
      TAU=FI/(OMEGA*(R-P))
      PUNCH 61,ID,REFI,E,R,FK1,FK2
      PUNCH 61,ID,REFI,E,FI,DPM,TAU
   14 AA=AA+ALP2
      AB=AB+BET2
      AFI=AFI+FK1
      AF2=AF2=FK2
      AD=AD+DPM
      AT=AT+TAU
      IF (J-6)9,15,15
   15 AE=AE+E
      AALP2=AA/Z
      ABET2=AB/Z
      AFK1=AFI/Z
      AFK2=AF2/Z
      ADPM=AD/Z
      ATAU=AT/Z
      AIMD2=2.0*3.14159/ABET2
      PUNCH 61, ID, CLMDA,AALP2,ABET2,AFK1,AFK2
      PUNCH 61,ID,CLMDA,AIMD2,ADPM,ATAU,CN
      GO TO 25
      END
```

APPARATUS

The apparatus used has been described adequately by Windle (20) and will not be discussed in detail. One modification should be noted, however. A water jacket around the sample cell was added by Chadwick[1] to aid in maintaining a constant dielectric temperature while calibration was in progress and data was being taken. After water had flowed through the jacket approximately one-half hour, the dielectric temperature maintained a constant temperature to within $\pm$ 1° C.

If measurements are desired as a function of temperature, it should be a simple matter to replace part of the water line by metal or glass wound with a heating coil which is connected to a variac. A temperature range of from below 20° to 40° or 50° C could then be maintained.

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[1]Curtis Chadwick installed the water jacket and took some data as part of a NSF undergraduate research project in physics at Kansas State University during the summer of 1961.

PROCEDURE AND RESULTS

The calibration procedures described by Windle (20) were used. Probe calibration was checked periodically but adjustment was never required. On the other hand, a calibration of the variable short was required each time the sample cell was installed and filled. This was necessary because of mechanical slack in the mechanism and because the electrical position of the short was slightly dependent on the temperature and concentration of the dielectric in the sample cell.

Calibration of the short was accomplished by setting the probe in the air filled wave guide at an odd multiple of $\lambda_1/4$ from the air-dielectric interface (20). The short was then moved until a minimum of the standing wave occurred at the probe. Three trials were made for each position of the short required for a minimum at the probe. The short was then moved to the next position for minimum signal at the probe. This procedure was repeated until the short had traversed the entire length of the dielectric or sample cell. As the distance between these positions of the short was $\lambda_2/2$ and each position was to a good approximation a distance $\frac{m\lambda_2}{4}$, m odd, from the interface, the position of the short could be calibrated by determining the corrected plunger reading,

$$\text{corrected reading} = \frac{2n+1}{2}\frac{\lambda_2}{2}, \quad n = 1, 2, 3, \ldots$$

and then by finding a correction factor to subtract from each apparent plunger reading. Thus, the correction factor = the average of the difference between the corrected plunger reading and the apparent plunger reading.

$$\text{c.f} = \text{average of (CRP - APR)}$$

All solutions were prepared by weighing on a chemical balance a small amount of the solute (nitrobenzene) and then mixing it with 100 ml of solvent (benzene). The number of polar molecules per cm^3 was then found from

$$N_1 = \frac{m\,N}{M(100\text{ ml solvent})} = m(4.8938 \times 10^{19})$$

where m is the number of grams of polar solute, N is Avogadro's number and M is the molecular weight of the solute.

Reagent grade thiophene free benzene was used for the solvent in all cases. Though benzene is often used as a reference liquid in dilute solution measurements, it is not ideal since it is difficult to remove any water which it may contain (5). No purification or water removal attempts were made though sodium ribbon could easily be placed in the benzene to aid in water removal. Reagent grade nitrobenzene was used as the polar solute. It too was used without additional purification. That the liquids were still quite pure may be implied from the Abbe refractometer readings on the pure liquids at 20° C and for the sodium D line.

Table 1. True and measured index of refraction

	measured	true[1,2]	difference
benzene	1.5008	1.50112	.0003
nitrobenzene	1.5520	1.55291	.0009
water	1.3326	1.3330	.0004

[1]Charles D. Hodgman, ed. Handbood of Chemistry and Physics. 36th edition. Chemical Rubber Company, 1954. pp. 760, 768.

[2]Henry Semat and Robert Katz, Physics. New York. Rinehart, 1958. p. 690.

The refractometer was calibrated using distilled water. These measured values were all corrected to 20° C by using a correction of -.0004/°C. As the thermometer was marked only to the nearest degree, it is felt the difference indicated in the third column of table 1 can be attributed entirely to uncertainties in temperature measurement and correction.

Dipole moment and relaxation times were calculated from the complex dielectric constant determined for different concentrations of nitrobenzene in benzene and for five different dielectric thicknesses at each concentration. Table 2 shows the data obtained from these measurements as well as the index of refraction at the sodium D line. The quantities shown in table 2 are the actual values punched on data cards and fed into the computer. The cutoff wavelength λ_c was also punched on input data cards but remained at 4.572 cm. All the symbols are defined on page 12.

Table 3 has been included to illustrate the nature of the results of each calculation. Whenever averages were computed, the ID number identifying the averages were the same as that of the last data card read by the computer.

The most important results, arranged in order of increasing concentration, are shown in table 4. Note μ for solutions numbered 526 and 527 is far out of line in comparison with the other values. A possible explanation is the measured refractive index for these solutions is in error. Reference to table 2 reveals n_D to be considerably higher for these solutions than for the others. The α_2 and k" values for solution 526 indicate other errors are present.

Table 2. Data obtained for each of five dielectric thicknesses of each concentration of nitrobenzene in benzene.

ID	D (cm)	TEMP °K	DX (cm)	XO (cm)	RNFI	PDEN $x10^{19}$
5011	7.975	293.5	.333	.350	1.5005	2.5839
5012	8.375	293.5	.248	2.161	1.5005	2.5839
5013	8.775	294.4	.750	1.420	1.5000	2.5839
5014	9.175	293.8	.333	.315	1.5003	2.5839
5015	9.575	292.0	.280	2.145	1.5012	2.5839
5101	7.966	291.6	.340	.322	1.5017	2.7846
5102	8.366	291.5	.292	2.16	1.5016	2.7846
5103	8.766	291.5	.058	1.42	1.5018	2.7846
5104	9.166	291.7	.342	.278	1.5018	2.7846
5105	9.566	291.7	.305	2.14	1.5016	2.7846
5151	7.945	292.2	.238	.432	1.5012	1.51218
5152	8.345	292.2	.172	2.22	1.5012	1.51218
5153	8.745	292.0	.365	1.58	1.5013	1.51218
5154	9.145	291.3	.238	.392	1.5016	1.51218
5155	9.545	291.3	.172	2.20	1.5016	1.51218
5211	7.931	291.8	.335	.395	1.5015	2.4714
5212	8.331	291.9	.238	2.202	1.5014	2.4714
5213	8.731	291.6	.665	1.525	1.5016	2.4714
5214	9.131	291.6	.398	.350	1.5016	2.4714
5215	9.531	291.6	.258	2.178	1.5016	2.4714
5221	7.927	291.0	.455	.213	1.5022	5.1385
5222	8.327	291.0	.460	2.11	1.5022	5.1385
5223	9.127	291.0	.500	.160	1.5022	5.1385
5224	9.527	291.0	.520	2.072	1.5022	5.1385
5225	7.127	291.0	.390	2.138	1.5022	5.1385
5231	7.926	290.5	.425	.308	1.5022	3.4403
5232	8.326	290.8	.358	2.148	1.5021	3.4403
5233	8.726	290.6	1.152	1.422	1.5022	3.4403
5234	9.126	290.6	.440	.250	1.5022	3.4403
5235	9.526	290.6	.402	2.122	1.5022	3.4403
5241	7.934	290.6	.255	.502	1.5019	1.4730
5242	8.334	290.6	.158	2.258	1.5020	1.4730
5243	8.734	290.6	.332	1.658	1.5020	1.4730
5244	9.134	290.6	.270	.462	1.5020	1.4730
5245	9.534	290.6	.172	2.232	1.5020	1.4730
5251	7.885	291.4	.485	0.278	1.5030	4.4338
5252	8.285	291.4	.388	2.155	1.5030	4.4338
5253	7.085	291.4	.350	2.178	1.5030	4.4338
5254	9.085	291.4	.480	0.225	1.5030	4.4338
5255	9.485	291.4	.455	2.125	1.5030	4.4338

Table 2. Continued

ID	D (cm)	TEMP °K	DX (cm)	XO (cm)	PEFI	PDEN x10^{19}
5261	7.900	291.5	.448	.318	1.5030	3.9542
5262	8.300	292.0	.352	2.175	1.5028	3.9542
5263	8.900	292.2	.928	.582	1.5027	3.9542
5264	9.100	292.4	.455	.272	1.5026	3.9542
5265	9.500	292.4	.425	.215	1.5026	3.9542
5271	6.696	290.6	.375	.428	1.5028	3.9523
5272	7.096	290.4	.250	2.232	1.5030	3.9523
5273	7.496	290.6	.635	1.605	1.5028	3.9523
5274	7.896	290.6	.430	.385	1.5028	3.9523
5275	8.296	290.7	.268	2.210	1.5027	3.9523
5281	7.909	290.5	.358	.465	1.5020	1.9477
5282	8.309	290.6	.230	2.255	1.5019	1.9477
5283	8.709	290.7	.515	1.672	1.5018	1.9477
5284	9.109	290.8	.345	.440	1.5018	1.9477
5285	9.509	290.9	.242	2.23	1.5017	1.9477
5291	7.913	290.7	.315	.418	1.5024	2.2080
5292	8.313	290.7	.205	2.23	1.5024	2.2080
5293	8.713	290.7	.585	1.59	1.5024	2.2080
5294	9.113	290.7	.335	.378	1.5024	2.2080
5295	9.513	290.7	.238	2.20	1.5024	2.2080
5301	7.961	290.8	.22	.440	1.5021	1.4630
5302	8.361	290.8	.15	2.24	1.5021	1.4630
5303	8.761	290.8	.362	1.590	1.5021	1.4630
5304	9.161	290.8	.230	.420	1.5021	1.4630
5305	9.561	290.8	.16	2.22	1.5021	1.4630
5381	7.966	290.4	.345	.265	1.5024	3.4526
5382	8.366	290.4	.330	2.12	1.5024	3.4526
5383	8.966	290.4	.730	.495	1.5024	3.4526
5384	9.366	290.4	.322	.028	1.5024	3.4526
5385	7.366	290.4	.438	1.878	1.5024	3.4526
5411	7.963	290.8	.392	.232	1.5023	4.0868
5412	8.363	290.8	.402	2.155	1.5023	4.0868
5413	8.963	290.8	.682	.440	1.5023	4.0868
5414	9.363	290.8	.358	.015	1.5023	4.0868
5415	7.363	290.8	.565	1.858	1.5023	4.0868
5481	7.961	291.4	.462	.142	1.5012	5.9142
5482	8.361	291.4	.630	2.05	1.5012	5.9142
5483	8.961	291.4	.730	.258	1.5012	5.9142
5484	6.961	291.4	.378	2.258	1.5012	5.9142
5485	7.761	291.4	.678	.345	1.5012	5.9142

Table 3. Typical values obtained in the computation of the dipole moment and relaxation time for solution No. 5h1; 8.53 mg/ml.

ID	E	SINE	A	B	
5h11	.2h4	.316	-.028	-.02h	
5h12	.2h9	.207	+.017	+.022	
5h13	.392	.573	-.0h4	-.0h4	
5h1h	.22h	.021	-.002	-.017	
5h15	.336	.536	+.053	+.0h4	
	ALP2	BET2	PK1	PK2	
5h11	.0h59	2.681	2.36h	.06h2	
5h12	.0554	2.683	2.366	.0775	
5h13	.0h21	2.687	2.372	.0590	
5h1h	.0h93	2.678	2.359	.0687	
5h15	.0h99	2.69h	2.381	.0700	
5h15	.0h85	2.685	2.368	.0679	
	R	P	PI	DPM debye	TAU x10-11
5h11	.3127	.29526	.0101	h.0h	.986
5h12	.3131	.29526	.0121	h.28	1.159
5h13	.31h0	.29526	.0092	h.0h	.839
5h1h	.3120	.29526	.0108	h.08	1.100
5h15	.3154	.29526	.0109	h.23	.922
5h15				h.15	1.001

Table 4. Results obtained for various concentrations of nitrobenzene in benzene.

ID	Density (mg/ml)	α_2	β_2	k'	k''	μ debye	τ 10^{-11} sec
530	2.99	.0193	2.643	2.312	.0265	4.68	.814
524	3.01	.0202	2.645	2.313	.0278	4.76	.814
515	3.09	.0206	2.652	2.323	.0284	5.01	.688
528	3.98	.0290	2.654	2.326	.0402	4.74	.950
529	4.53	.0284	2.664	2.340	.0394	4.62	.795
521	5.05	.0315	2.662	2.337	.0437	4.47	.877
501	5.28	.0317	2.657	2.330	.0439	4.34	.938
510	5.69	.0351	2.665	2.341	.0487	4.36	.943
527	5.97	.0385	2.672	2.352	.0535	3.81	.956
523	7.03	.0448	2.680	2.362	.0625	4.37	.969
538	7.06	.0419	2.678	2.359	.0585	4.25	.948
526	8.08	.0221	2.686	2.370	.0310	3.95	.489
511	8.53	.0485	2.685	2.368	.0679	4.15	1.00
525	9.06	.0554	2.694	2.381	.0777	4.21	1.04
522	10.50	.0602	2.698	2.386	.0846	4.05	1.05
548	12.08	.0666	2.710	2.404	.0941	4.01	1.01

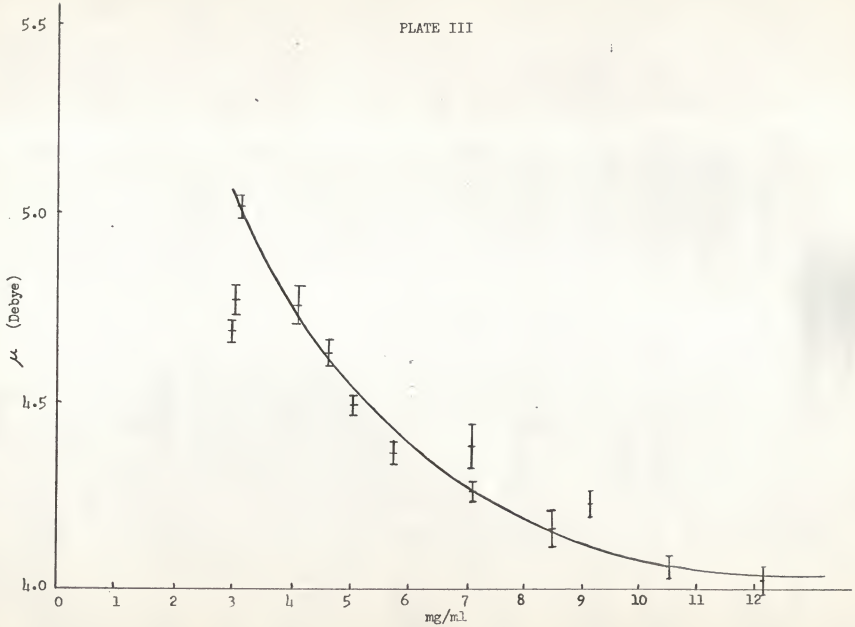
Plate III is a graph of the dipole moment values in table 4 as a function of concentration. Points for solutions 526 and 527 have been ignored.

When a small correction factor was added to n_D, the calculated value of μ changed radically, especially at the lower concentrations. Plate IV shows the variation of dipole moment with concentration for correction factors of 0.000, 0.010, 0.013, and 0.017. Corrected μ values for the point at 12.08 mg/ml were not available. Points which were far out of line with the others were omitted for clarity though more data should be taken to further justify the omission of the points.

EXPLANATION OF PLATE III

Variation of dipole moment with concentration of solution.

PLATE III



EXPLANATION OF PLATE IV

Dipole moment verses concentration with a correction factor added to N (N + CN) as parameter.

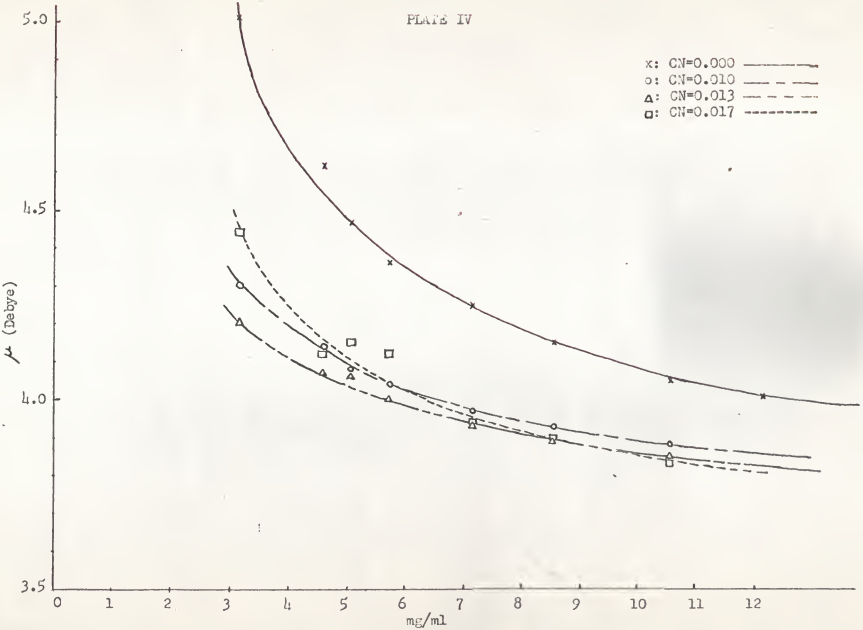
x: CN = 0.000

o: CN = 0.010

Δ: CN = 0.013

□: CN = 0.017

PLATE IV


x: CN=0.000
o: CN=0.010
Δ: CN=0.013
□: CN=0.017
μ (Debye)
5.0
4.5
4.0
3.5
0
1
2
3
4
5
6
7
8
9
10
11
12
mg/ml

Values of R, P and R - P are shown in table 5 and R - P is plotted against the concentration in Plate V. Plate V also shows the effect on R - P of adding .013 and .015 to the index of refraction. As R is a function of k' and k'' which are determined for each dielectric thickness and P is a function of n_D only and is dependent on the temperature, average values of R and P are meaningless. Therefore, just the first value of R and P for each concentration was used.

An error in the expression for R was discovered in the 650 computer program. Consequently, computations of μ and τ made by the 650 computer were incorrect. Plate VI shows the effect this error had on the calculated value of μ, the upper curve corresponding to the incorrect value of R. The results of data taken by Chadwick[1] are shown as calculated by each computer. The circles represent points computed by Windle (20).

Table 6 shows the recomputed values of μ and τ originally computed by Windle (20) on the 650 computer. The R of equation (26) has been corrected in these calculations.

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[1]Chadwick, op. cit.

Table 5. R, P and R - P values.

Density mg/ml	ID	R	P	R - P
2.99	5301	.3044	.2952	.0092
3.01	5241	.3040	.2951	.0089
3.09	5151	.3059	.2947	.0112
3.98	5281	.3067	.2951	.0116
4.53	5291	.3089	.2954	.0135
5.05	5211	.3078	.2949	.0129
5.28	5011	.3065	.2944	.0121
5.69	5101	.3085	.2950	.0135
5.97	5271	.3107	.2955	.0152
7.03	5231	.3113	.2952	.0161
7.06	5381	.3111	.2953	.0158
8.08	5261	.3144	.2956	.0188
8.53	5411	.3127	.2953	.0174
9.06	5251	.3151	.2956	.0195
10.50	5221	.3157	.2952	.0205
12.80	5481	.3176	.2947	.0229

EXPLANATION OF PLATE V

Variation of (R - P) with concentration

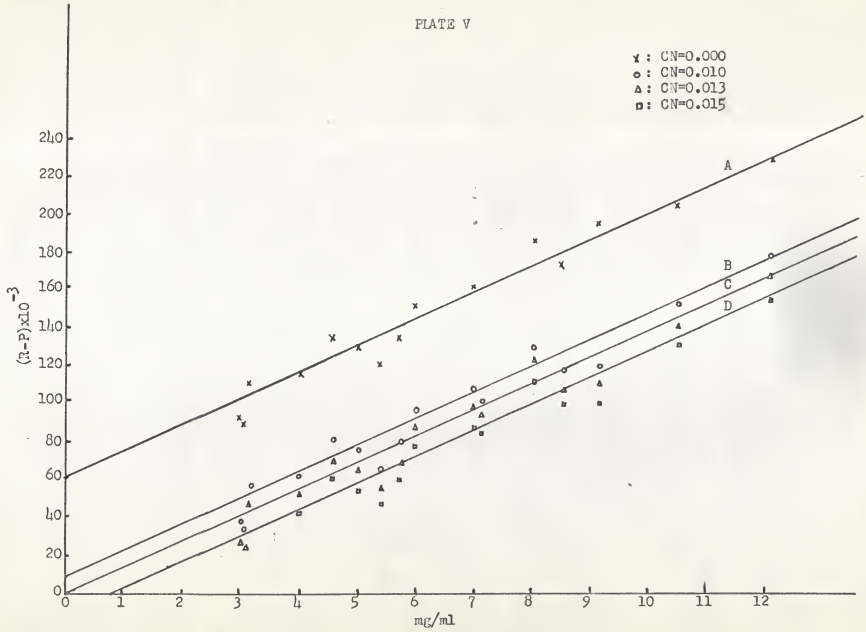
Curve A: CN = 0.000

Curve B: CN = 0.010

Curve C: CN = 0.013

Curve D: CN = 0.015

PLATE V


x : CN=0.000
o : CN=0.010
Δ : CN=0.013
□ : CN=0.015
A
B
C
D
(R-P)x10⁻³
mg/ml
0
20
40
60
80
100
120
140
160
180
200
220
240
1
2
3
4
5
6
7
8
9
10
11
12

EXPLANATION OF PLATE VI

Variation of dipole moment with

concentration of solution.

Curve A. $R = \frac{k'^2 + k' + k'' - 2}{(k' + 2)^2 + k''^2}$

Curve B. $R = \frac{k'^2 + k' + k''^2 - 2}{(k' - 2)^2 + k''^2}$

Note k'' was not squared in the numerator of R for Curve A. See equations (27).

PLATE VI

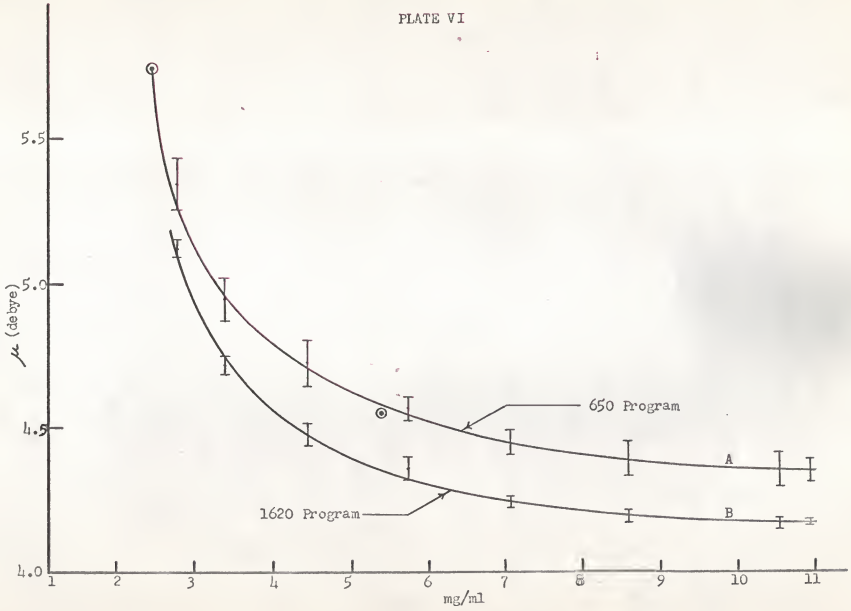

5.5
5.0
4.5
4.0
μ (debye)
650 Program
1620 Program
A
B
1
2
3
4
5
6
7
8
9
10
11
mg/ml

Table 6. Dipole moment and relaxation time for various materials.

Molecule	density mg/ml	τ x10^{-12}sec	μ Debye	values in literature
Acetone	15.84	2.09	2.85	2.85[1], 2.75[2] (16)
	7.92	2.01	3.05	2.87 - 2.89[1] (9)
	3.92	1.65	4.48	3.04[3] (3)
	1.98	1.91	3.89	2.72 - 2.78 (18)
Acetonitrile	7.83	2.35	3.49	3.94[1], 3.4 - 3.5 (16)
	3.92	2.71	3.70	3.8 - 4.0[1] (9)
	1.96	2.47	4.13	3.2 - 3.6[3] (6)
Dimethylamine	14.22	2.46	2.39	.91, 1.13[2] (16) (18)
	7.11[4]	2.11	2.08	.89 - .95[1] (9)
	3.56	2.80	2.49	
	1.78	1.92	3.59	
Nitrobenzene	17.41	10.86	3.81	3.51, 3.22 (16)
	10.93	7.76	3.97	3.92 (19)
	5.68	7.11	4.29	3.90 - 4.05 (18)
	2.55	10.69	4.45	

[1]Values obtained in vapor state.
[2]Values obtained in solution.
[3]Obtained using apparatus and method similar to that used in this work.
[4]Average of 4 sets of data.

DISCUSSION

The reader is referred to other works for a thorough discussion of errors (20) (16) (10) (11).

The Debye equation (24) was derived for gases only and under the assumption the polar molecules are so far apart they exert negligible forces on each other. This paper describes dilute solutions of polar molecules in a nonpolar solvent. In the limit of infinite dilution it was assumed that the polar molecules in liquids were also far apart from each other there was no mutual interaction. However, as the dipole moment was a function of concentration, it was evident the molecules did interact. Moreover, measurements in the limit of infinite dilution were not possible because attenuation due to wall losses and other side effects became significant and could not be ignored, but k_{min} could not be determined because it became so small it fell below the noise level.

Presumably one could say extrapolation to infinite dilution eliminated both dipole-dipole interaction and also dipole-solvent interaction called the solvent effect. Nevertheless, the Debye and Lorentz field treatment gives rise to dipole moment calculations from solution data which differ from measurements made on gases. Although no modification to date has been entirely satisfactory, Onsager and Kirkwood made the first fundamental progress in remedying the deficiencies in the Lorentz field (5).

In spite of this difficulty the Debye theory is still often used for measurements on dilute solutions. Plate III gives an extrapolated value of $\mu = 4.15 \pm 0.05$ for infinite dilution; Plate VI indicates $\mu = 4.18$. Some Nitrobenzene dipole moment values in the literature are 4.2 (1), 4.08 (11), 4.24(2), 3.9 - 4.1 (16), 3.93 (13) and 3.92 (19).

When these are contrasted with the vapor values of 4.23 (16) it is seen there is close agreement.

Additional criticism of the Debye equation as applied to liquids has the substitution of n^2 for k. As has been mentioned, n_D^2, where n_D is the index of refraction at the sodium D line, has often been used along with a dispersion formula to extrapolate to infinite wavelength. In this way only the electronic polarization was obtained, the atomic polarization being ignored as it is less than 10% of P_e (11) (12). Also, dispersion regions are known to exist for benzene and nitrobenzene in infrared and centimeter wavelength regions (14) (7). But measurements in the submillimeter region are very limited (5) and it is possible that dispersion formulas applied to the centimeter through submillimeter region would yield a more precise value for the total induced polarization.

The method of finding the induced polarization used by this writer was direct substitution of n_D^2 for k. Debye (4) argued this was valid since P_e for n_D was greater than P_e for λ_∞ and thus partial compensation was made for the neglect of P_a. Foley (14) estimated the error in making this assumption was not much more than one percent. But once the dipole moment of a substance is known, perhaps by means of another method such as application of the Stark effect (17), the Debye equation can be used to find the total induced polarization and hence, as was the case in this paper, the index of refraction in the centimeter wavelength region.

From the theory of dispersion it is seen an increase in n should occur when an absorption band is passed through from a shorter to a longer wavelength. Plate V shows the effect on of adding small correction factors to the index of refraction. The entire curve became

flatter and lower, as the dipole moment decreased more for the lower concentrations than for the higher concentrations. Thus the extrapolated dipole moment value is lower and more in line with the majority of solution values. A correction factor of .013 gave a curve which was quite flat and when extrapolated to infinite dilution gave $\mu = 4.04$ D which was well within the range of values in the literature. As the correction factor was increased beyond .013, μ at low concentrations started to rise, quite rapidly in some cases, indicating an optimum correction factor had been passed. At moderate dilution μ continued to decrease very slowly as the correction was increased past .017. For this reason it was the .013 curve which was extrapolated to zero concentration. The drop and then rise of the curve can best be seen by following the movement of μ for a given concentration as the correction factor is increased.

Plate V gives a more vivid example of the effect of adding a correction to n. Separation of the complex Debye equation into real and imaginary parts gives

$$R - jI = P + \frac{4\pi\mu^2 N_1}{9KT(1 + \omega^2\tau^2)} - j\frac{4\pi\mu^2 N_1}{9KT(1 + \omega^2\tau^2)} \qquad (28)$$

For the real part we have

$$R - P = \frac{4\pi\mu^2}{9KT(1 + \omega^2\tau^2)} N_1 \qquad (29)$$

Plate V is a graph of this equation; the plotted points fall along a straight line as one would expect if τ were not a function of the concentration N_1 as table 4 shows it is. But over the limited range of concentrations considered here, one may assume τ to be constant. T must be constant and is nearly so; τ is a function of T also.

At zero concentration the right side of equation (29) is zero and hence R - P must also be zero. This condition is easily obtained by adding a correction factor of approximately .013 to n_p. Note, however, the relaxation time, equation (26), is still a well behaved function and takes the indeterminable form 0/0.

Assuming τ to be constant, the slope of the graph of equation (29) yields the dipole moment. With T = 291° K and $\tau = 8.93 \times 10^{-12}$ sec., the value obtained for μ is 3.97 D. It appears, then, this is a valid method for obtaining a corrected refractive index which is at least equivalent to the index obtained by a dispersion formula. In addition, the corrected index corresponds to the frequency used in measuring k^2 (16) making it unnecessary to know the often poorly established absorption coefficients as is required in many dispersion formulas.

Early results were obtained with an IBM 650 computer. Later, the 650 was replaced by an IBM 1620 computer. This change necessitated rewriting the computer program for the new machine. During the rewriting, preceding theses were used as a guide, and when the new program did not give results identical with what had been obtained before, a close examination was made of each step in the derivation of each equation and in each step of both the old and new computer programs. As a result several typographical errors were found in the equations in several of the theses. These errors were not present in the 650 computer program.

More important, however, was the discovery of an error in the 650 computer program in the formation of R of equations (27). The expression for R is repeated here for convenience as

$$R = \frac{k'^2 + k' + k''^2 - 2}{(k' + 2)^2 + k''^2}$$

In the 650 program, k'' in the numerator was not squared. Consequently the computed values for both μ and τ were in error. The data taken by Windle (20) has been recalculated and the new μ and τ values are presented in table 6. It should be mentioned the crystal detector response law assumed by Windle for his nitrobenzene measurements was not known with certainty.

For nitrobenzene in benzene, the index of refraction should increase uniformly with an increase in the concentration of nitrobenzene. In table 7 refractive index values were corrected to 290° K and compared with concentration. Column five is n_D corrected to 290° K by using a correction of -.0005/C°; column six is the corrected index using -.0004/C° as the correction factor. As considerable variation was found to exist, it became evident a graphical method of determining n_D might be more appropriate. For benzene and nitrobenzene the indices of refraction are additive and hence a precise and carefully constructed straight line graph would have given more precise and consistent index determinations.

Though the Debye equation used here does not take into account all the effects necessary in a precise theory, the results from the Debye equation differ little from those of more precise theory. On the other hand, once a precise dipole moment value is established for a polar liquid, it is here indicated the Debye equation can be used to find the total induced polarization, the atomic polarization and hence the refractive index of that polar liquid which corresponds to extrapolation to "infinite wavelength" in the far infrared as is done with dispersion formulas but without the need to know the number and intensities of the absorption bands.

Table 7. Check on Index of Refraction

ID	Density mg/ml	N_D measured	T °K	N at 290°K -.0005/C°	N at 290°K -.0004/C°
530	2.99	1.5011	292.8	1.5025	1.5022
524	3.01	1.5019	290.6	1.5022	1.5021
515	3.09	1.5012	292.2	1.5023	1.5021
528	3.98	1.5018	291.0	1.5023	1.5022
529	4.53	1.5030	290.0	1.5030	1.5030
521	5.05	1.5015	291.8	1.5024	1.5022
501	5.28	1.4973	299.8	1.5022	1.5012
510	5.69	1.4976	299.8	1.5025	1.5015
527	5.97	1.5028	290.6	1.5031	1.5030
523	7.03	1.5025	290.0	1.5025	1.5025
538*	7.05	1.5016	292.0	1.5026	1.5024
526	8.08	1.5038	290.0	1.5038	1.5038
511*	8.53	1.5020	291.6	1.5028	1.5026
525	9.06	1.5038	289.8	1.5037	1.5037
522	10.50	1.5027	290.0	1.5027	1.5027
518*	12.08	1.4999	294.0	1.5019	1.5015

*Average of two readings corresponding to two "focus" settings of Abbe Refractometer.

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MICROWAVE MEASUREMENTS OF THE ELECTRIC DIPOLE MOMENT AND OTHER DIELECTRIC PROPERTIES OF NITROBENZENE

by

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Microwave standing waves of three centimeter wavelength were measured to determine the propagation factor required for the solution of a complex impedance equation and complex impedance equation was expandéd into a first order Taylor series in two variables and solved by iteration. In this way the complex dielectric constant of nitrobenzene was determined. The nitrobenzene was contained in an upright sample cell fitted with a plunger mechanism whereby the thickness of the nitrobenzene dielectric could easily be varied. A water jacket surrounded the cell and running tap water helped maintain a constant dielectric temperature.

The propagation factor was used to determine the complex dielectric constant in the complex Debye equation from which dipole moment calculations were made.

Measurements were made at five different dielectric thicknesses and an average dipole moment and relaxation time was computed. Data was taken on various concentrations of nitrobenzene in a benzene solvent and the dipole moment of nitrobenzene was plotted against concentration.

An IBM 1620 digital computer was used to solve the impedance equation, compute the dipole moment and relaxation time and to average the results in sets of five. A correction was made on the Windle computer program.

Index of refraction measurements for the sodium D line were used to determine the induced polarization in the Debye equation. An increase of approximately one percent in the index of refraction was shown to yield dipole moment values in line with those obtained by use of dispersion formulas required to extrapolate refractive index measurements at the sodium D line to a value which it should be for the Maxwell relation $n_D^2 = k^\infty$ to hold at the frequency for which k^∞ was determined.

A graphical method was used to indicate the required correction to add to the measured sodium D line refractive index.

It appears, then, one can obtain an empirical correction factor to add to the index of refraction at the sodium D line and obtain the index of refraction for nitrobenzene which corresponds to the index extrapolated to the far infrared region by use of dispersion formulas but without the need to know the number and intensities of the absorption bands in the infrared.